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ASD-TDR-62-322
Part II

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PHENYLENE SULFIDE POLYMERS

TECHNICAL DOCUMENTARY REPORT NO. ASD-TDR-62-322, Part II
December 1962

Directorate of Materials and Processes
Aeronautical Systems Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

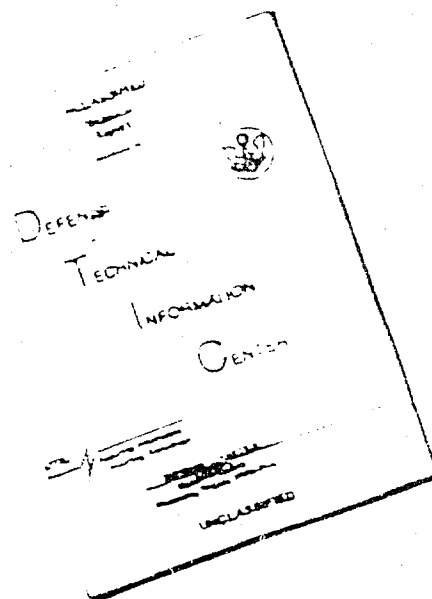
Project No. 7340, Task No. 734004

(Prepared under Contract No. AF 33(616)-7251 by The Dow Chemical Company, Midland, Michigan; Harry A. Smith and Carl E. Handlovits, Authors)

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FOREWORD

This report was prepared by The Dow Chemical Company under USAF Contract No. AF 33(616)-7251. This contract was initiated under Project No. 7340, "Non-Metallic and Composite Materials", Task No. 734004, "New Organic and Inorganic Polymers". The work was administered under the direction of the Directorate of Materials and Processes, Aeronautical Systems Division, with Mr. G. A. Loughran acting as project engineer.

This report covers work conducted from March 1962 to December 1962.

This report was prepared by Dr. Harry A. Smith, Project Director. The laboratory work was conducted by Dr. Harry A. Smith, Carl E. Handlovits, William K. Carrington and James B. Louch. The administrator of the contract is Dr. W. R. Nummy, Director of the Polymer Research Laboratory.

ABSTRACT

The investigation of phenylene sulfide polymers has been divided into seven areas of endeavor. These are monomer synthesis, polymerization studies, large scale preparations, physical properties of the linear polymer, chemical properties of the polymer, crosslinking studies, and applications. With improvements in the monomer synthesis and polymerization, one pound batches of polymer can be readily made. Once made, the polymer has a degree of polymerization in excess of 100 and is inert to air up to 300°C. It can be chemically crosslinked to improve its stability at 400°C in air or heat treated to not only improve its thermal and oxidative stability at 400°C but to improve its properties as well. The polymer can form fibers from the melt and be used in coatings and laminates. However, its most thoroughly investigated property is its adherence. Bond strengths up to 2700 psi have been obtained on 17-7 stainless steel. It also adheres well to glass and aluminum.

This technical documentary report has been reviewed and is approved.

William E. Gibbs

WILLIAM E. GIBBS
Acting Chief, Polymer Branch
Nonmetallic Materials Laboratory
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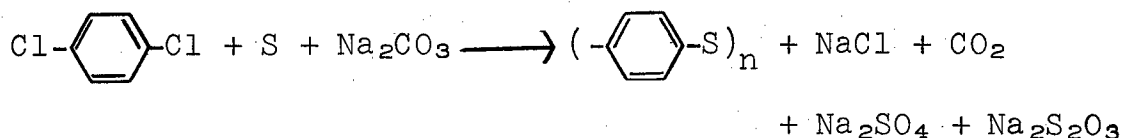
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I. INTRODUCTION

The purpose of this work is to obtain a useful plastic material which is thermally stable. The initial work on phenylene sulfide polymers was done by Dr. A. D. Macallum of London, Ontario. He discovered that this polymer could be prepared by the sequence of reactions shown below.



Macallum Polymerization

Since Dow makes *p*-dichlorobenzene and the other two starting materials are inexpensive, the patents for this work were purchased from Dr. Macallum by The Dow Chemical Company in 1954. Subsequent studies were carried on in the Plastics Department Research Laboratories.

It soon became apparent that the Macallum polymerization would be a difficult reaction to control since the yields and the polymer properties were very unpredictable. In addition the polymeric material obtained was somewhat branched and/or lightly crosslinked, and containing a portion which was an insoluble, infusible highly crosslinked material. Consequently, it was decided to prepare a more readily characterizable polymer namely a linear polymer from the condensation polymerization of such species as *p*-halothiophenoxides.

Through the data obtained from a kinetic study of model reactions, polymerization studies, and monomer synthesis it was possible to determine the monomer most likely to result in high molecular weight linear phenylene sulfide polymer. This monomer was cuprous *p*-bromothiophenoxide. Further work on this monomer has shown that degrees of polymerization, based on melt viscosity and end group analysis, of 100-200 can be obtained by solid state or solution polymerization. The polymer is stable in air or nitrogen to 400-450°C and has useful polymeric properties. In addition, a thermal treatment can convert it to a more stable species having decidedly improved properties.

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II. RESULTS AND DISCUSSION

In the course of the investigation to prepare linear phenylene sulfide polymers, seven different aspects of the problem were studied. These were: (1) monomer synthesis, (2) polymerization studies, (3) large scale preparations, (4) physical properties of the polymer, (5) chemical properties, (6) crosslinking, and (7) applications.

Monomer Synthesis

The monomer synthesis is a two step process starting from thiophenol. The first step involves reaction of thiophenol with bromine to give bis-(p-bromophenyl) disulfide as shown in figure 1.

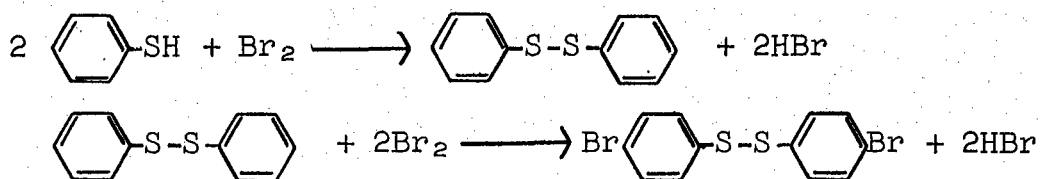


Figure 1. Synthesis of Bis-(p-bromophenyl) Disulfide

Since the reaction is carried out in the absence of solvent, the product is obtained as a solid cake. To avoid formation of a cake so as to facilitate recovery of the bis-(p-bromophenyl) disulfide, several solvents have been used to carry out the bromination reaction such as water, methylene chloride, and carbon tetrachloride. In each case low yields of impure material resulted. Consequently it was decided to use agitation only to prevent formation of the solid cake.

The second step in the synthesis of the monomer, cuprous p-bromothiophenoxide, is the reaction of the disulfide obtained in the first step with copper dust. Several variables associated with this reaction have been investigated. One of these was the effect of the type of copper dust used. The results of this study are presented in Table I. Comparing runs made under similar conditions it can be seen that there is little difference between electrolytic dust, surface activated electrolytic dust, and freshly prepared copper dust. There are, however, appreciable differences between these materials and hydrogen purified electrolytic dust and electrolytic powder. In the case of the hydrogen purified material residual hydrogen is probably the cause of the observed results. Hydrogen present would reduce the

TABLE I

The Effect of Type of Copper Dust
on the Monomer Synthesis

<u>Run</u>	<u>Copper Dust</u>	<u>Time (hrs.)</u>	<u>Temperature (°C)</u>	<u>% Excess Disulfide</u>	<u>Conver- sion (%)</u>
1	Freshly Prepared ^a	96.0	119	10	96.8
2	Freshly Prepared ^a	22.5	119	50	99.0
3	Freshly Prepared ^a	68.0	78	10	~40.0
4	Electrolytic Dust (Hydrogen reduced)	360.0	119	10	45.0
5	Electrolytic Dust	22.5	119	50	93.5
6	Electrolytic Dust	96.0	78	10	~30.0
7	Electrolytic Dust ^{b,c} (Surface activated)	26.5	119	50	91.7
8	Electrolytic Dust ^d (Surface activated)	25.5	119	50	90.5
9	Electrolytic Powder	168.0	119	50	37.2

a. Made from Copper Sulfate by Zinc-Acid Reduction.

b. Shaken with steel balls - 35 minutes.

c. Average of two runs.

d. Shaken with steel balls - 90 minutes.

bis-(p-bromophenyl) disulfide to p-bromothiophenol rendering it incapable of reaction with copper metal and thereby resulting in low conversions. In the case of the electrolytic powder, the particle size is the culprit. Photomicrographs indicate that the electrolytic dust has particle sizes of 2-10 μ while the powder is 20-50 μ . This larger size drastically reduces the surface area of the material which thereby reduces the reaction rate as observed.

A second variable studied in the copper disulfide reaction was the effect of solvent. The results of these investigations are depicted in Table II. From the results it can be seen that solvent polarity seems to favor the use of n-alkyl alcohols. This is indicated by the higher melting points, higher yields and the brighter yellow color obtained for monomers made in these solvents as compared to those from other solvents. In addition, the reaction is somewhat faster in alcohols, the lower boiling n-butyl alcohol producing essentially the same yield of monomer in the same time as the higher boiling hydrocarbon and glycol. Amines and halogenated aliphatics are apparently undesirable due to reaction of the solvent with the reagents.

Another variable considered was pyridine catalysis. These results are listed in Table III. From runs 3-5 and 6-8 it can be seen that once pyridine is present it exerts only a small concentration dependent rate enhancement effect. A much larger effect is shown in runs 7 and 8 where the difference is the presence and absence of pyridine. Runs 1 and 2 indicate somewhat anomalous results, but these may be due to some side reactions which would result in the low melting points observed.

In addition to the above investigations, the effects of changes in the reaction conditions were also studied. One of these was the effect of temperature. Table IV shows the results for this variable. The data indicate that temperatures between 80° and 170°C can be used successfully to prepare monomer if pyridine or lutidine are not used as solvents.¹ Above 170°C the monomer will polymerize to low molecular weight polymer as shown by the n-octyl alcohol reaction and by prolonged reaction in n-heptyl alcohol. This latter fact may be of some use if an attempt is made to produce polymer from monomer formed in situ. Between 80° and 170°C the reaction rate for monomer production increases with increasing temperature. The reaction in n-amyl alcohol, however, appears to be slower than the trend of reaction rates should indicate. This is due to the lower concentration of bis-(p-bromophenyl)disulfide used in this reaction compared to the other reactions. The toluene reaction appears to be faster than the trend would indicate. This is due to the high pyridine concentration used in this reaction.

TABLE II

Effect of Solvent on Monomer Preparation

<u>Reaction Conditions</u>			<u>Monomer</u>		
<u>Solvent</u>	<u>Time (hrs.)</u>	<u>Temperature (°C)</u>	<u>M.P. (°C)</u>	<u>Yield (%)</u>	<u>Color</u>
Ethanol	68-96	78	----	~30-40	Yellow
Benzene	72	79	----	0.0	-----
m-Xylene	144	130	274.5-275	96.8	Bright Yellow
Ethylene Glycol	144	130	272	82.8	Greenish Yellow
n-Butyl Alcohol	18-144	119	277.5-278	95-100	Bright Yellow
n-Amyl Alcohol	82	139	277-277.5	93.6	Bright Yellow
Ethanol Amine	192	139	Reacts		
1,1,2,2 Tetrachloro- ethane	24	147	Reacts		

TABLE III

Effect of Pyridine on Monomer Synthesis

<u>Run</u>	<u>Mole Ratio Pyridine/ Disulfide</u>	<u>Excess Disulfide (%)</u>	<u>Reaction Time (hrs.)</u>	<u>Yield (%)</u>	<u>M.P. (°C)</u>
1	1.00	10	168	97.2	259 - 263
2	0.94	10	120	97.2	254 - 257
3	0.91	10	96	99.8	274.5-275
4	0.18	10	120	86.6	277.5-278
5	0.013	10	216	100.0	277.5-278
6	1.00	50	23	99.0	-
7	0.32	50	24	99.0	-
8	0.00	50	236	100.0	-

TABLE IV

The Effect of Temperature on
Monomer Synthesis

<u>Solvent</u>	<u>Reaction Temp. (°C)</u>	<u>Reaction Time (hrs.)</u>	<u>Pyridine/ Disulfide</u>	<u>Excess Disulfide (%)</u>	<u>Yield (%)</u>	<u>M.P. (°C)</u>
Benzene	79	72	1.00	10	0	-
n-Propyl Alcohol	95	184	1.00	50	97.0	278-278.5
Toluene	110	21	4.00	0	100.0	274-275
n-Butyl Alcohol	115	23	1.00	50	99.0	277-278
n-Amyl Alcohol	138-139	80	1.00	10	93.6	277-278
n-Hexyl Alcohol	150-153	5	1.00	50	97.0	275-276
n-Heptyl Alcohol	165-170	5	1.00	50	94.0	274-275
n-Heptyl Alcohol	172-152	96	0.00	50	Some polymer	
n-Octyl Alcohol	192-203	144	0.00	50	Polymerized	

Since cleavage of disulfide bonds can be light activated, the effect of light on the reaction rate was studied. This was of interest also because it was suspected that the ultraviolet radiation in sunlight had catalyzed the reaction on several occasions. Therefore several reactions were run under irradiation by a G.E., UA-2, photochemical lamp. The results of these experiments are listed in Table V. As in Table IV a temperature effect is shown by the difference in the reaction rate when using benzene and chlorobenzene as solvents. The biggest difference, however, is that between irradiated and non-irradiated chlorobenzene reactions which show a three-fold rate enhancement with light. Ultraviolet light does appear to catalyze the reaction.

Another reaction condition variable studied was the bis-(p-bromophenyl) disulfide concentration.

As shown in Table III, runs 1, 4, 6, and 7, use of a 50% excess of bis-(p-bromophenyl) disulfide can drastically reduce reaction time from 5-7 days to one day or less. The excess bis-(p-bromophenyl) disulfide used can be recovered on work up of the reaction and subsequently be reused. This procedure has reduced substantially the time needed to prepare polymer from the original reagents, thiophenol and bromine.

In a further attempt to reduce the polymer preparation time an attempt was made to prepare monomer from bis-(p-bromophenyl) disulfide made in situ and not isolated. This would eliminate the remaining bottleneck in the polymer process, the bis-(p-bromophenyl) disulfide purification. The preparation of the above disulfide was carried out in the usual manner using carbon tetrachloride as the solvent. However, instead of isolating the material it was washed with sodium bisulfite while still in solution. Then *n*-butyl alcohol was added and the carbon tetrachloride stripped off. To the resulting solution the copper dust was added and the monomer preparation reaction carried out as usual. This procedure resulted in a 94% yield of monomer melting somewhat low at 268.5-269.0°C. Therefore, with some further effort on this reaction sequence it might be developed into an acceptable procedure for monomer preparation.

Polymerization Studies

Several of the variables effecting polymerization have been investigated. One of the factors studied was the effect of air on the polymerization. The purpose of this study was to determine if air was deleterious to the polymerization and more specifically was it responsible for the formation of bis-(p-bromophenyl) disulfide observed in some of the polymerizations. To ascertain this information two sets of experiments were made.

TABLE V

Effect of Light on Monomer Preparation

<u>Solvent-Temperature</u> <u>(°C)</u>		<u>Time to Complete Reaction</u>	
		<u>No Light</u>	<u>Light</u>
Benzene	79	No Reaction	6 days (35-40% completion) 3 days (25% completion)
Chlorobenzene	132	6 days	2 days
n-Butyl Alcohol	119	6 days	Reacts

One, Table VI, was a series of polymerizations for 9 days at 200°C in the presence of varying amounts of air. The second, Table VII, was three 24 hour polymerizations under oxygen, air, and argon.

From the data in Table VI the actual amount of air present seems to have little correlation with the results observed.

The data in Table VII was obtained to answer the question about bis-(p-bromophenyl) disulfide formation. As the table indicates, none of this disulfide was found. Therefore, oxygen or air is not the cause of its occurrence. Oxygen, however, does appear to accelerate polymerization, but in addition, it appears to interact with the polymer as indicated by the change in the color of the reaction mixture. The bis-(p-bromophenyl)disulfide, then, is probably produced by air oxidation of residual monomer after opening of the reaction bombs. In other words, it indicates an incomplete reaction due to insufficient reaction time.

In some of the polymerizations, evidence of crosslinked polymer was found. One source for this crosslinking would be a polybrominated monomer. This material could be formed as a result of excess bromine being used in the preparation of bis-(p-bromophenyl) disulfide. Therefore, some disulfide was prepared using only an equivalent amount of bromine. However, polymerization of monomer from this source resulted in a low yield of poor quality polymer. Apparently, either an equivalent amount of bromine is not sufficient to produce bis-(p-bromophenyl) disulfide or else some polybrominated monomer is needed to get high molecular weight or to act as polymerization initiators.

Temperature was another polymerization variable which was investigated. The results of polymerizations at varying temperatures are presented in Table VIII. As the data indicate 300°C is too high a temperature for polymerization. Temperatures from 200° to 250°C are satisfactory with the best results being obtained at 200°C as indicated by the color, yield, and especially the melt viscosity. It is conceivable that temperatures below 200°C would result in even better properties, however, the reaction time would be extremely long.

During the course of scaling up the polymerization reaction it was found that the larger the quantity of monomer used the longer the reaction time became to give melt viscosities over 1000 poises. It was believed that since the bombs were not agitated that the above result could be due to poor heat transfer in the polymer. This would cause the central portions of the polymer mass to take longer to reach reaction temperature and thus slow down the overall reaction as observed. To verify this hypothesis, four reactions were carried out in capped iodine

TABLE VI

Effect of Air During Polymerization
on Polymer Properties

<u>Sample</u>	<u>Total Pressure (mm Hg)</u>	<u>Air Pressure (mm Hg)</u>	<u>Polymer Yield (%)</u>	<u>M.P. (°C)</u>	<u>η_{303} (poises)</u>	<u>η_{rel}</u>
1	5×10^{-5}	5×10^{-5}	-	275-277	~ 65	-
2	760	1×10^{-4}	64	280-286	136	1.149
3	10^{-2}	10^{-2}	48	279-283	~ 40	-
4	0.15	0.15	55.6	279-283	~ 50	1.123
5	1	1	32.6	280-283	~ 50	1.144
6	50	50	24.6	279-283	~ 50	1.130
7	760	760	86.0	283-286	440	1.169
8	760	760	62.5	280-288	$3.2 \times 10^{+4}$	1.169

TABLE VII

The Effect of Oxygen Concentration
on the Polymerization Reaction

<u>Run</u>	<u>Oxygen (%)</u>	<u>Reaction Mixture Color</u>	<u>Disulfide Yield (%)</u>	<u>Remarks</u>
1	100	White	0	Mostly polymer
2	20	Pale Yellow	0	Some polymer
3	0	Yellow	0	Mostly monomer

TABLE VIII

Effect of Polymerization Temperature on

Polymer Properties^a

<u>Temperature</u> <u>(°C)</u>	<u>Time</u> <u>(Days)</u>	<u>Yield</u> <u>(%)</u>	<u>M.P.</u> <u>(°C)</u>	<u>Color</u>	<u>η_{303}</u> <u>(poises)</u>
200	6	80-90	285-289	Light Grey	$1.0 \times 10^3 - 8.0 \times 10^4$
225	6	78	283-293	Grey	-----
250	6	80-90	284-287	Grey to Brown	$1.0 \times 10^2 - 6.0 \times 10^3$
300	6	18 ^b	240-245	Black	-----

a. Diphenyl Ether Soluble Polymers.

b. Low yield due to large quantity of insolubles.

flasks containing an argon atmosphere in an oven at 200°C. Iodine flasks were used since it would allow small runs to be spread out in the flask bottom in a thin layer. Thus, heat transfer would not be a problem in these cases. The reaction mixtures were loaded in the flasks under an argon atmosphere in a dry box. The data obtained are shown in Table IX. In general the results are poor. In all cases the reaction mixtures turned brown during the reaction period. Both of these results suggest the presence of an impurity which was probably introduced from the dry box atmosphere (naphthalene or phosphoric acid vapor from the drying agents). However, the experiment did give the desired information since the six gram runs lost their bright yellow monomer color in 2-3 days whereas the 98 gram reaction took about a week. The larger reaction mixture had one advantage over the other runs in that its lower surface area per gram and smaller gas space reduced the amount of contamination that it suffered from the dry box atmosphere. This would result in a higher melting point as observed.

A short cursory investigation of possible light catalysis of polymerization was made. Irradiation of monomer with ultraviolet light for six days in refluxing chlorobenzene produced no polymer. This was the result of either too low of a reaction temperature or the lack of catalysis by ultraviolet light. Furthermore, no difference has been noted between reaction times of monomer polymerized in the dark and that exposed to light. Therefore, light does not appear to be an important factor in polymerization.

In an effort to improve the ease of carrying out the polymerization, an experiment was conducted whereby monomer was polymerized in a petri dish in a vacuum oven at 200°C under an argon atmosphere. Polymerization time was 20 days. The polymer was obtained in a 100% yield and having the following properties.

M.P. 281-285°C

DPO Solubles 69%

$\eta_{303} 1.1 \times 10^4$

Other than the high quantity of diphenyl ether insolubles this material is very much like polymer produced in the usual manner. This technique is being pursued further.

In addition to studies on the polymerization itself some investigations on the polymer isolation and purification processes were also carried out.

TABLE IX

Iodine Flask Polymerizations

<u>Monomer Charge</u> <u>(gms)</u>	<u>Reaction Time</u> <u>(days)</u>	<u>Yield</u> <u>(%)</u>	<u>M.P.</u> <u>(°C)</u>
6.2	5	41.1	200-235
6.1	9	43.4	235-246
6.2	9	49.3	218-238
98.3	9	48.4	260-273

One type of extraction process used for polymer isolation and purification is diphenyl ether extraction. In this process the crude polymer mixture is boiled in diphenyl ether. The "linear" polymer present dissolves leaving the insoluble cross-linked polymer and cuprous bromide behind as a residue after filtration. The soluble polymer is then precipitated by pouring the hot solution with stirring into methanol or acetone. It was found in this process that a trace of acid preferably hydrochloric acid aided in the filtration of precipitated polymer by enhancing coagulation of the polymer particles. In addition it was found to be undesirable to precipitate the polymer by cooling in diphenyl ether since this produced a polymer containing occluded diphenyl ether which could not be removed by drying for 48 hours at 158°C and 10 mm of mercury. The boiling point of diphenyl ether is 120°C so that free solvent should have been removed under the drying conditions.

In an effort to obtain a more facile work up procedure, extraction with concentrated ammonium hydroxide and later concentrated hydrochloric acid were investigated. Both reagents were used to extract cuprous bromide from the crude polymer product. If successful, a cuprous bromide free mixture of linear and possibly crosslinked polymer would remain. Since both of these reagents were used to accomplish the same purpose a comparative investigation of their ability to extract cuprous bromide was made. These results are expressed in figure 2. As it can be seen, cuprous bromide dissolves very rapidly in concentrated hydrochloric acid, 15 grams dissolving in 100 ml in 5 minutes or less. In concentrated ammonium hydroxide, even with 300 ml, solution of 15 grams takes over 15 minutes. Consequently the cuprous bromide can be removed from the polymer much more quickly by concentrated hydrochloric acid extraction. In addition the solubility of cuprous bromide in the two reagents, 30.5 gms/100 ml in concentrated hydrochloric acid and 14.7 gms/100 ml in concentrated ammonium hydroxide, favors the use of hydrochloric acid also.

Of further interest in figure 2 are the results with the monomer, cuprous *p*-bromothiophenoxide. This material is almost insoluble in concentrated ammonium hydroxide but dissolves and/or reacts quite rapidly in concentrated hydrochloric acid (15 grams in about 20-25 minutes). This is a further advantage in the use of hydrochloric acid since monomer removal from the polymer will result in a higher average molecular weight.

Since there was some question about the acid resistance of the polymer, a sample of polymer was stirred for one hour in concentrated hydrochloric acid. This material showed no significant change in any of its properties. Stirring another polymer sample in concentrated hydrochloric acid for one hour followed by heating at 60-70°C for one hour and then repeating produced essentially no change in the properties of the polymer either.

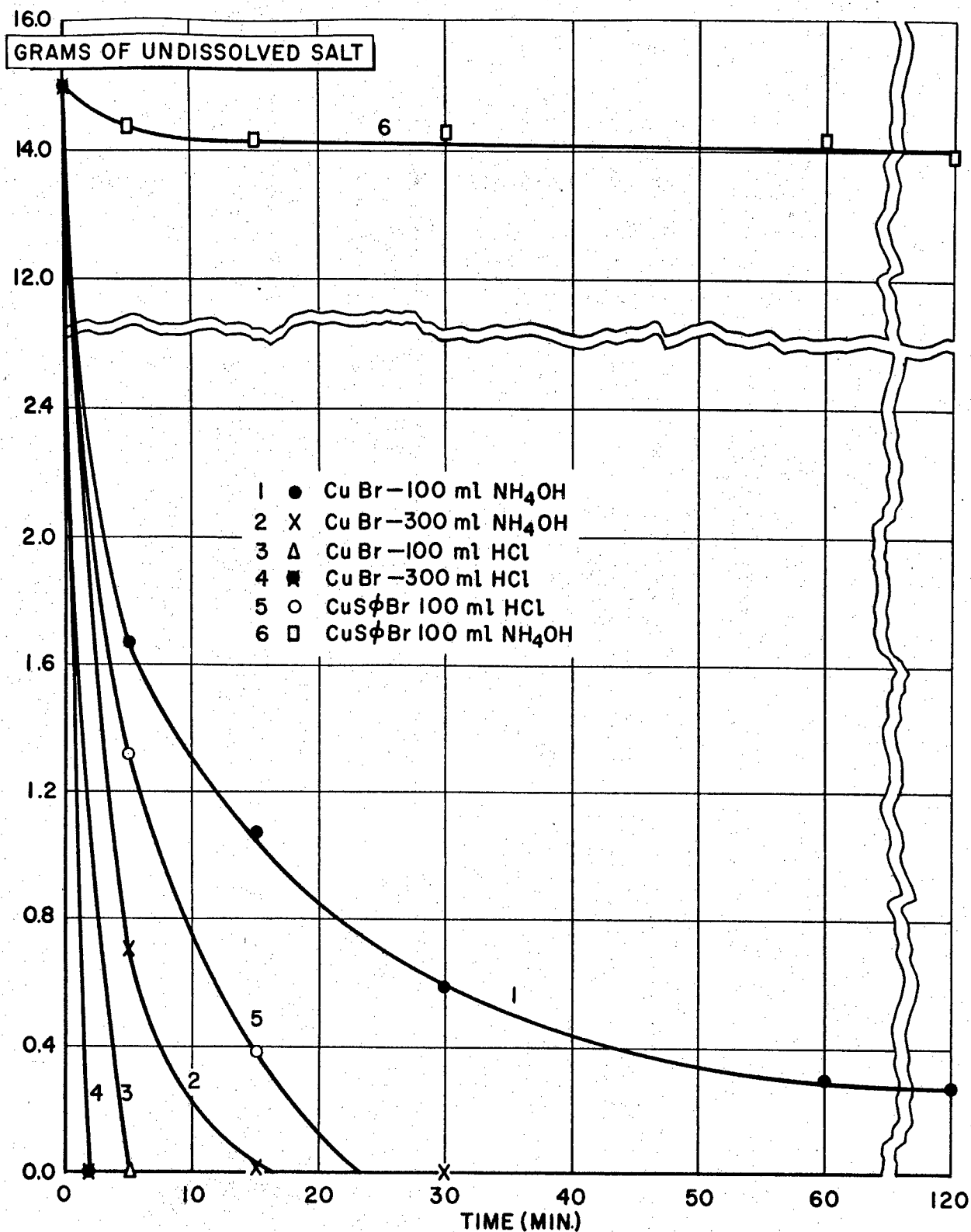


FIG. 2

RATE OF SOLUTION OF CuBr AND CuSφBr

It was found recently that it was possible to analyze a polymer sample in such a way that inorganic copper and bromine could be distinguished from their organic counterparts. This would be desirable from the standpoint of knowing when hydrochloric acid or ammonium hydroxide extraction was sufficient. The method used for analysis by the analytical laboratory was extraction of polymer-cuprous bromide mixture by concentrated ammonium hydroxide followed by analysis of both extract and residue for copper and bromide. However, this technique did not result in complete removal of the cuprous bromide from the samples studied. In addition comparison of the results with the known mixtures showed that removal of some of the copper end groups must have occurred also. Therefore, this method would be unable to give exact results but could indicate that the level of cuprous bromide present in a sample is less than 1%. Perhaps better results, at least from the standpoint of bromine analysis, could be obtained using the hydrochloric acid extraction mentioned above since it should result in more complete removal of cuprous bromide.

Large Scale Polymer Preparation

In general few problems have been encountered in scaling up the preparation process. The procedures used have been essentially as previously reported in WADD TR 61-139 and ASD-TDR-62-322.

About 35 pounds of bis-(p-bromophenyl) disulfide have been prepared in 5-6 pound batches in the usual way². Once purified this has been converted to monomer in about three pound batches³. Reaction times were about three days. No difficulty was encountered in the scale up of these two reactions.

The first problem encountered in the scale up arose in the purification of bis-(p-bromophenyl) disulfide because of the large quantity of solvent required on this scale of preparation. In addition the recrystallization solvent used, absolute ethanol, had a low flash point which introduced a serious safety hazard in this large an operation. Both problems have been alleviated by a change to 100-140°C Skelly Solvent. This material has a much higher flash point and only requires 15-16 liters of solvent for two recrystallizations of about 3 pounds of bis-(p-bromophenyl) disulfide with an 85-95% recovery of purified material. Ethanol would require 30-35 liters for the same amount of bis-(p-bromophenyl) disulfide with at best a 70-80% recovery of purified material.

Another materials handling problem arose in the polymer isolation and purification step. If a diphenyl ether soluble material free of any cuprous bromide was desired, 20-30 gallons

of diphenyl ether and 60-90 gallons of methanol would be required for one pound of polymer. In addition the best procedure requires pouring a diphenyl ether solution at 225-250°C into cold methanol (B.P. 65°C).

A somewhat better procedure is extraction of the cuprous bromide from the polymer with concentrated ammonium hydroxide. This requires only 8-10 gallons of solvent to remove cuprous bromide to about a 1-2% level. In addition the polymer unlike diphenyl ether soluble material may contain partially crosslinked polymer.

A still better technique as far as materials handling, time required, and efficiency of operation is concerned, is concentrated hydrochloric acid extraction of the cuprous bromide from the polymer. As the previous discussion under polymerization studies has indicated this technique could reduce the quantity of solvent required to 3-5 gallons per pound of polymer and at the same time could allow the extraction time to be reduced to one third (Figure 2). This technique reduces the residual cuprous bromide level to 0.5-2.0% after 1-2 extractions. Again the polymer may contain partially crosslinked material.

Of the three methods only the diphenyl ether technique gives cuprous bromide free polymer at the present time. The other two methods are preferable from a materials handling and safety point of view and theoretically should be capable of producing cuprous bromide free polymer also. With our present analytical techniques as a check on removal of cuprous bromide a closer approach to this theoretical possibility should be achievable. Therefore, a facile workup procedure to obtain cuprous bromide free polymer is possible using the cuprous bromide extraction procedures coupled with analysis.

In the scale up of the polymerization reaction two alternatives presented themselves. One was a large scale solution reaction and the second a melt reaction. The results of the first attempts at the scaling up of these reactions are given in ASD-TDR-62-322, p. 25, 31, and 32. A further attempt to carry out a large scale solution reaction has been made since then. This resulted in essentially the same type of product as the two previous solution polymerization experiments. In other words a low molecular weight polymer was obtained, and as before the glass bomb liner had broken probably during assembly of the bomb.

Much better results were obtained with the solid state polymerizations. This data is presented in Table X. Yields and polymer properties are fairly consistent over the whole series of runs. A few interesting points should be discussed, however. Most of the melt viscosities listed are for diphenyl ether soluble

TABLE X

Large Scale Polymerizations

Run	Bomb Charge (gms)	Time (days)	Temperature (°C)	Yield ^c (%)	M.P. (°C)	DPO Solubility (%)	η 303° (poises)	η rel ^d
1	106.0 ^a	9	200	100	280-290	81.0	8.0 x 10 ^{4d}	1.148
2	106.0 ^a	9	200	100	280-290	81.0	1.42 x 10 ^{3d}	1.172
3	125.0 ^a	9	200	100	280-283	74.6	1.7 x 10 ^{3d}	1.178
4	88.5 ^a	14	200	100	285-288	81.0	1.3 x 10 ^{3d}	1.192
5	319.0 ^b	9	200	60 ^e	280-285	70.0	3.9 x 10 ^{2d}	1.125
6	319.0 ^b	14	200	89	282-287	62.6	2.0 x 10 ³	1.187
7	319.0 ^b	14	200	83	282-287	81.2	1.3 x 10 ^{3d}	1.191
8	319.0 ^b	14	200	83	282-287	81.2	1.9 x 10 ^{3d}	1.186
9	320.0 ^a	14	200	96	285-287	91.0	3.1 x 10 ²	1.197
10	320.0 ^a	20	200	100	283-285	86.8	2.5 x 10 ^{2d}	1.192
11	320.0 ^a	25	200	100	285-288	84.2	6.0 x 10 ⁴	1.206
12	320.0 ^a	26	200	100	285-288	86.8	6.0 x 10 ^{4d}	1.216
13	325.0 ^a	21	200	100	281-285	65.6	3.5 x 10 ⁴	1.219
							4.7 x 10 ⁴	1.210
							4.8 x 10 ⁴	-----
							4.8 x 10 ^{4d}	-----

a. Argon atmosphere.

b. Air atmosphere.

c. Theoretical yield is 43% of charge weight.

d. Data from diphenyl ether soluble material.

e. 40% BrØSSØBr was found in the crude polymer.

material. In some of the runs, runs 1 and 3, melt viscosities of the ammonium hydroxide extracted materials were obtained which were 100-1000 times greater than those listed. This was undoubtedly due to either the presence of crosslinked polymer or both crosslinked polymer and occluded cuprous bromide. However, it should be noted in runs 6-10 that there is essentially no difference between the melt viscosities of the ammonium hydroxide or hydrochloric acid extracted polymer and the diphenyl ether soluble polymer. Consequently, these polymers must contain very little if any crosslinked polymer or occluded cuprous bromide after extraction by the ammonium hydroxide or hydrochloric acid. Run 13 was interesting in that the hydrochloric acid extracted polymer appeared to crosslink and gel at the polymer melting point unlike previous samples. It is believed that the polymer became contaminated while drying in the vacuum oven. This could have been caused by some material that had sublimed into the oven from previous material that had been dried in that oven. While trying to duplicate the material in this polymer it was discovered that a large amount, >5%, of cuprous bromide in a polymer can cause similar results. Analytical results on the above sample show only 0.87% copper so that the maximum amount of cuprous bromide present would be about 2% and therefore insufficient to produce the results observed. Therefore, the contamination theory seems more plausible at the present time. The diphenyl ether soluble material from run 13 does not gel at the melting point.

The results from run 5 show the effects of two of the problems encountered in scaling up the solid state polymerization reaction. In this run 40% of the solid material recovered from the reaction proved to be bis-(p-bromophenyl) disulfide, the remaining 60% being the polymer as indicated in Table X. This run was made under an air atmosphere because the polymerization experiments with air present, Table VI, had indicated that this would not be detrimental. Consequently, when this large quantity of bis-(p-bromophenyl) disulfide was obtained, it prompted some questions as to the validity of the results in Table VI. Therefore, when the experiments in Table VII confirmed the results in Table VI by showing that air present during polymerization was not the cause of the bis-(p-bromophenyl) disulfide formation, an investigation was made to determine what did cause this result.

An alternative cause of the bis-(p-bromophenyl) disulfide formation could be an incomplete reaction coupled with air oxidation of the residual monomer during workup. This hypothesis is strengthened by the fact that run 5 had the shortest reaction time and was the only unagitated run of the larger scale polymerizations in Table X. In addition no bis-(p-bromophenyl) disulfide was found in any of the other runs immediately after opening of the reaction containers prior to workup. However, in the series of runs under argon the one having the shortest reaction time,

run 9, did contain 2-3% of monomer. This showed up as bis-(p-bromophenyl) disulfide which precipitated during workup. The reason that disulfide is produced from monomer during workup is that the workup procedure converts the monomer to the more readily oxidized thiophenol which can then be air oxidized to disulfide. Therefore, it seems that this first problem, formation of bis-(p-bromophenyl) disulfide from residual monomer, is actually a result of the second problem encountered in large scale runs. This problem is slow reactions due to poor heat transfer through the reaction mixture (Table IX). Agitation of the reaction mixtures during polymerization can alleviate this difficulty. At present hand agitation is being used but a mechanical agitation system is being studied. Thus it appears that with agitation both problems encountered during polymerization on a large scale can be eliminated or reduced.

It was interesting to note that the 2-3% monomer found in run 9 would indicate a degree of polymerization for this polymer of 42 by condensation polymerization kinetics. A melt viscosity determination indicated a degree of polymerization of 46 while end group analysis indicated 44. All of these values are in excellent agreement and indicate that the determinations of molecular weight by melt viscosity based on end group analysis are on a firm foundation.

"Linear" Polymer Properties

In addition to a continuing study of the various polymers produced from the aspect of solution and melt viscosity some other properties of phenylene sulfide polymer have been investigated. One of these is the solubility characteristics of the "linear" polymer. The results of this study are presented in Table XI. The results indicate that in order for a solvent to dissolve the polymer, it must be capable of being heated to over 200°C. This requirement is undoubtedly due to the crystalline nature of the polymer. In addition to the boiling point requirement the best solvents appear to be those having a cohesive energy density of 90-100.

Because of the above solubility properties of the polymer conventional methods of absolute molecular weight determination were not available. It was thought that due to the low precipitation temperature of the polymer in 1-methylnaphthalene, that a light scattering instrument that could operate at 150°C could be used to determine molecular weight. However, it was found that on standing at 150°C the polymer precipitates, making this method useless.

TABLE XI

Solubility of Phenylene Sulfide Polymers

<u>Solvent</u>	<u>Solubility at Reflux</u>	<u>Precipitation Temperature</u>
Pyridine	0.0%	-----
2,4-Lutidine	0.0%	-----
Toluene	0.0%	-----
<u>o</u> -Dichlorobenzene	0.0%	-----
Polyether	0.0%	-----
Sulfuric Acid	Reacts	-----
Diphenyl Ether	$\geq 2.0\%$	200°C
Diphenyl Sulfide	$\geq 1.0\%$	170°C
Nitrobenzene	$\geq 1.0\%$	175°C
1-Methylnaphthalene	$\sim 5.0\%$	145°C

The other classical methods, boiling point elevation and freezing point depression did not work because solvents were not available that both would dissolve the polymer and had a large enough molal elevation or depression factor, as the case may be, to allow measurement of the molecular weight.

The only absolute method left was end group analysis. While this appeared to be fairly reliable for degrees of polymerization less than 60-70 where the per cent bromine is greater than 1%, it became unreliable beyond these limits. Therefore, it was necessary to resort to relative molecular weight methods which could be calibrated with end group analysis in the region where this was reliable.

One of the relative methods used was melt viscosity. In order to avoid any error due to occluded cuprous bromide in the polymer, all samples used to establish the relationship between melt viscosity at 303°C and degree of polymerization from bromine end group analysis were diphenyl ether soluble materials⁴. Any diphenyl ether insoluble materials present in the original polymer, were filtered off from the hot diphenyl ether solution prior to precipitation in methanol. Thus not only were the samples free from cuprous bromide but they were also essentially linear polymers. Therefore, bromine analysis could be directly related to degree of polymerization by the relation:

$$(1) \quad \overline{D.P.}_{Br} = \frac{80-81 (\% Br/100)}{108 (\% Br/100)} \quad (\text{Reference 5})$$

The melt viscosity can be determined using the relationship derived by Small⁶ for the type of apparatus that was used to determine the values in Table XII^{7,8}.

$$(2) \quad \eta = \frac{F f(y)}{S^2}$$

where: η = melt viscosity in poises

F = force exerted by the viscometer plunger in dynes

$$= F (\text{gms}) \times 9.8 \times 10^2$$

$f(y)$ = instrument constant
(8.2×10^{-3} in our instrument)

S = slope of plot of plunger penetration in centimeters versus square root of time in seconds

The data obtained for the purpose of deriving the correlation between melt viscosity and end group analysis are presented in Table XII and Figure 3. The log log plot of this data lies reasonably well along a straight line, Figure 3, from which the equation relating melt viscosity and degree of polymerization can be obtained. This relationship is:

$$(3) \log M_n = 0.147 \log \eta_{303} + 1.32$$

where: M_n = number average molecular weight based on
bromine end group analysis

η_{303} = melt viscosity at 303°C in poises

With this relationship established and if the melt viscosity is known, then the molecular weight of a polymer sample can be determined. Even samples containing cuprous bromide below a 3-4% level can be determined using this technique since that quantity of cuprous bromide does not affect the melt viscosity appreciably. Crosslinked materials, if present in large enough amounts, can also produce high melt viscosity results, and therefore, it is always wise to determine the viscosity of the diphenyl ether soluble materials from any polymer in order to determine whether any error in the molecular weight due to an excessively high melt viscosity could be present.

Generally little or no error from these sources has been observed in the large scale preparations, but some high results have been observed with smaller runs due to the presence of 10-20% of crosslinked polymer in the material before diphenyl ether extraction.

A second relative molecular weight determination method was solution viscosity. These determinations are made on only diphenyl ether soluble materials since insolubles by giving the wrong solution concentration or by plugging the capillary could cause viscosities that are low or high. Since the melt viscosity molecular weight relationship has already been established, solution viscosity can be correlated either with molecular weight directly or through a correlation with melt viscosity. Table XII could enable either relationship to be made while Figure 4 utilizes the second of the two approaches. Since there were more samples of polymer on which both melt and solution viscosities had been determined than those which had bromine analyses, Figure 4 has several points²⁴ on it not listed in Table XII. Again the data on the log log plot fit very closely to a straight line from which the following equation can be derived.

TABLE XII

Melt Viscosity versus End Group Analysis

<u>Sample</u>	<u>% Cu</u>	<u>% Br</u>	<u>D.P._{Br}</u>	<u>η_{303} (poises)</u>	<u>η_{rel}</u>
1	0.015	4.6	16	3.5	-----
2	0.006	2.04	36	20	1.138
3	0.016	1.60	45	20	1.173
4	0.003	2.1	34	50	1.149
5	0.006	2.35	31	60	1.144
6	0.006	2.31	31	61	1.132
7	0.00	1.9	38	75	1.143
8	0.015	1.9	38	113	1.155
9	0.09	1.4	52	132	1.194
10	0.00	1.7	43	133	1.166
11	0.00	2.1	34	140	1.149
12	0.8	2.8	26	200	1.124
13	-----	1.5	48	200	1.137
14	-----	1.3	56	251	1.192
15	0.21	1.6	45	260	1.138
16	-----	1.5	48	313	1.197
17	0.00	1.4	52	440	1.169
18	<1	1.18	62	550	1.186
19	0.05	1.3	56	770	1.240
20	0.09	1.49	49	900	1.201
21	0.01	1.2	61	1100	1.254
22	1.7	2.3	31	1300	1.192
23	-----	0.86	85	1400	-----
24	-----	0.79	93	1400	-----
25	0.27	1.56	47	1700	1.195
26	0.015	1.2	61	1700	1.182
27	<1	1.18	62	1700	1.186
28	0.18	0.68	108	1800	1.239
29	<1	1.18	62	1900	1.196
30	<1	1.65	44	2000	1.187
31	0.04	1.12	65	4000	1.198
32	0.13	1.14	64	7500	-----
33	-----	0.84	87	60,000	1.216
34	0.46	0.45	165	230,000	-----

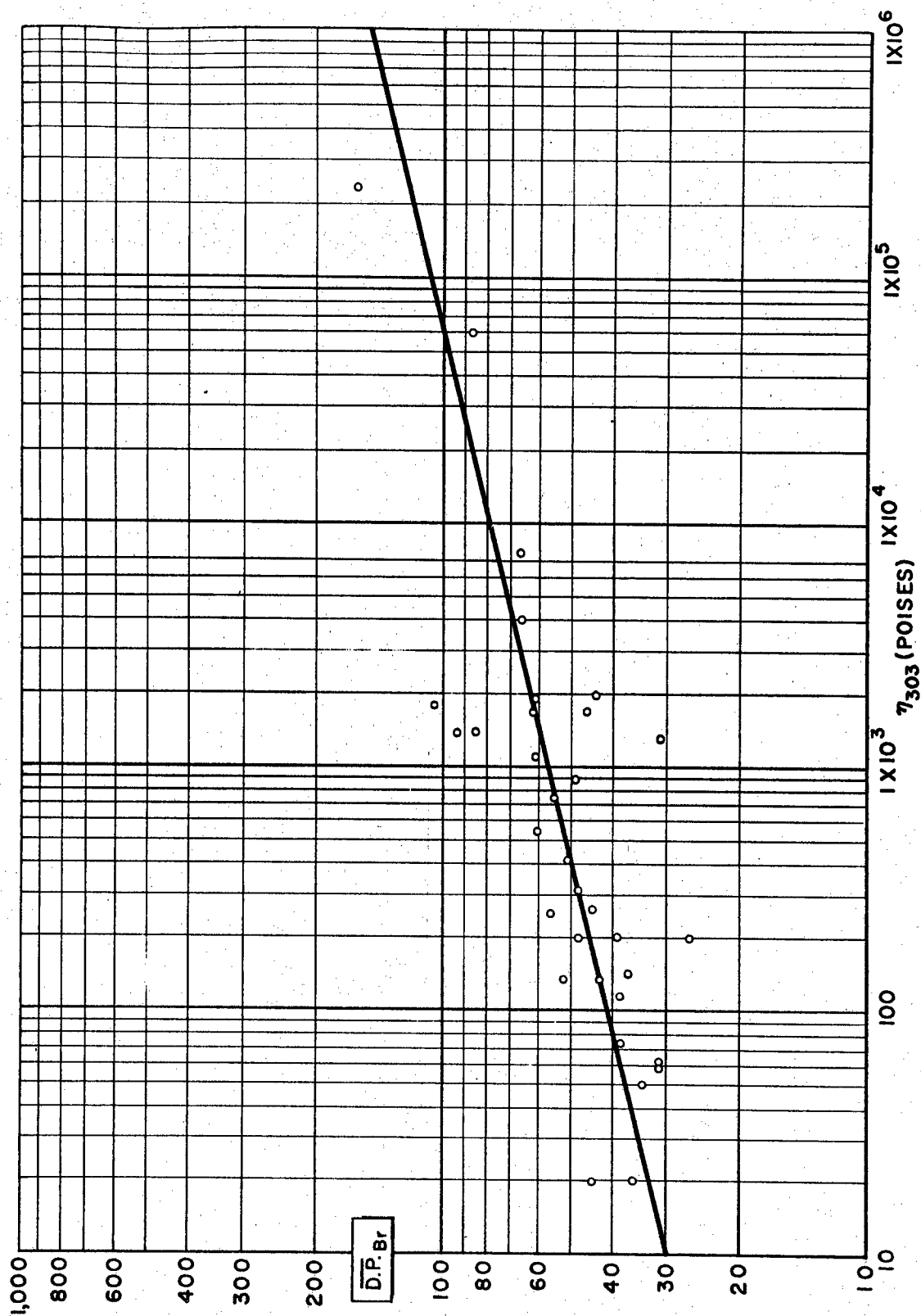


FIG. 3
RELATIONSHIP OF MELT VISCOSITY TO $\overline{D.P.}_{Br}$

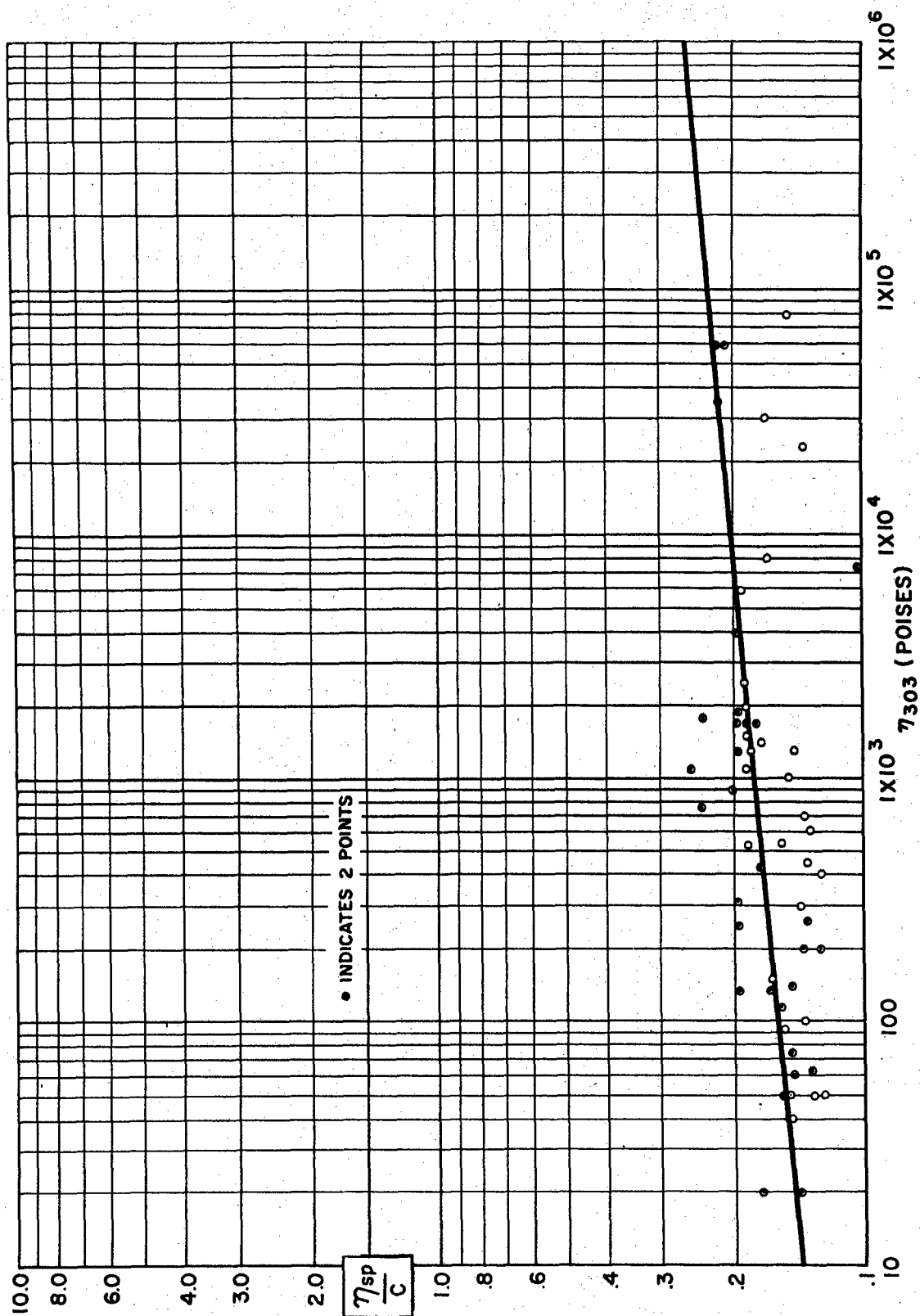


FIG. 4

RELATIONSHIP OF MELT VISCOSITY TO SOLUTION VISCOSITY

$$(4) \quad \log \frac{\eta_{sp}}{C} = 0.0603 \log \eta_{303} - 0.936$$

where: η_{sp} = specific viscosity

C = concentration of polymer solution
(gms/100 ml)

η_{303} = melt viscosity at 303°C in poises

Using this relationship (equation 4) and equation 3, solution viscosity can be related directly to molecular weight as shown in equation 5 where the symbols have the same significance as previously defined.

$$(5) \quad \log M_n = 2.43 \log \frac{\eta_{sp}}{C} + 3.60$$

Since the data were available in Table XII for determining this relationship (equation 5) directly, this was done also in Figure 5. This plot leads to essentially the same relationship with the slope constant of the line being 2.35 and the intercept 3.47. These results are very close to the 2.43 and 3.60 values in equation 5 and along with the good fit of the data to their respective curves indicate that the correlations presented in equations 3-5 seem to be quite reliable.

Another property of the polymer investigated was the variation of polymer film properties with melt viscosity or molecular weight. The results of this somewhat cursory study indicates a break in a viscosity property curve occurring at about 1.3×10^3 poises on the melt viscosity scale. Below this viscosity, properties rapidly deteriorate. Above this, the properties improve but only gradually with increasing viscosity. Therefore viscosities in excess of 1.3×10^3 poises would be required in order to obtain the best possible polymer properties. Using the relationship between melt viscosity and molecular weight described previously (equation 3) the break in viscosity would indicate a molecular weight of 6500.

An examination of the solvent resistance of the polymer is being conducted. The preliminary but incomplete results indicate that the polymer is very resistant to solvents such as methanol, carbon disulfide, and methylene chloride.

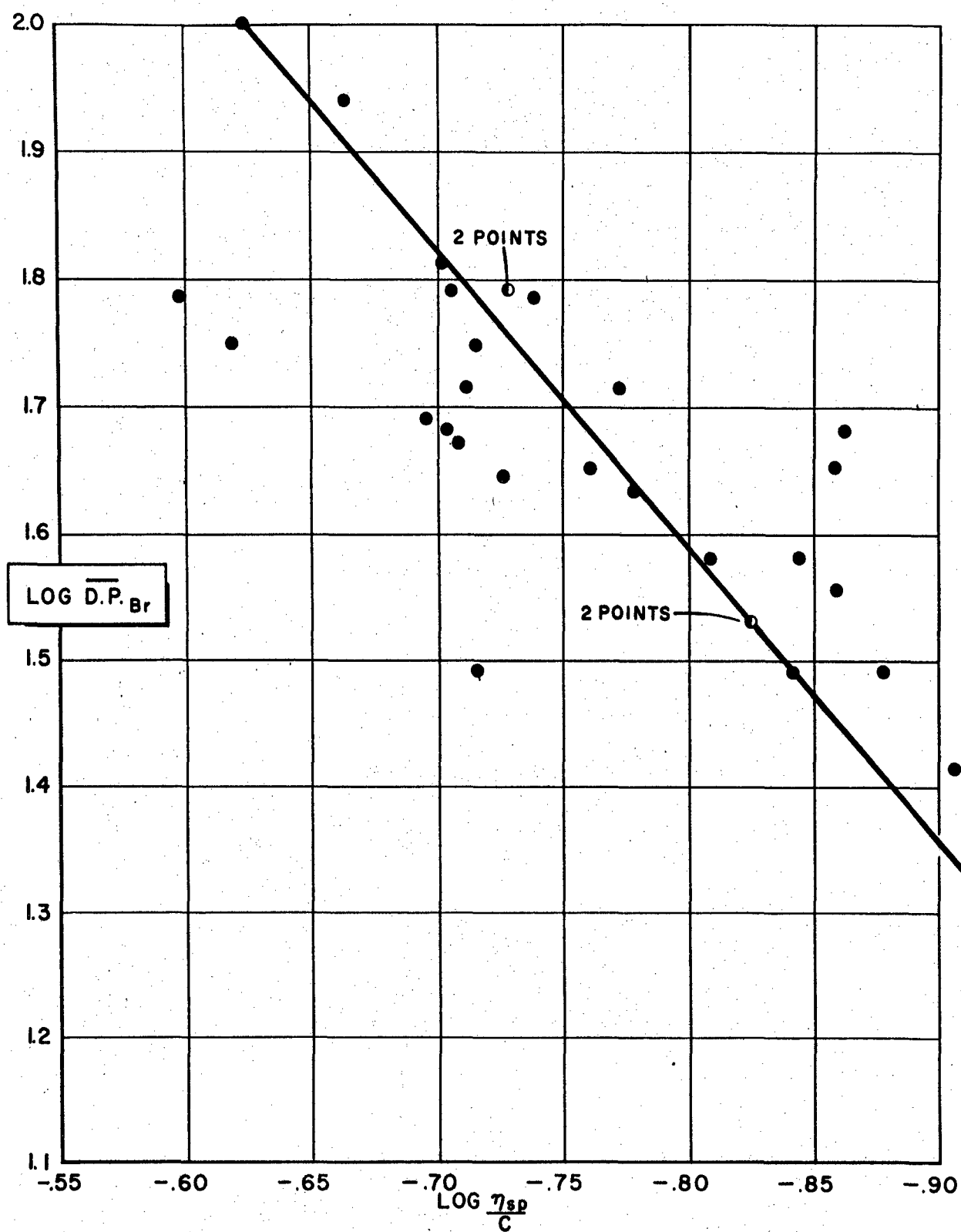


FIG. 5

SOLUTION VISCOSITY VERSUS $\overline{D.P.}_{Br}$

Chemical Properties of the Polymer

Three chemical properties of the polymer were investigated. Two of these, the effect of heat and chemical crosslinking will be discussed later. The third property concerns the ability of the polymer to be oxidized.

Since it was believed that oxidized forms of sulfur such as the sulfoxide or sulfone might be more stable than the sulfide, it was desired to study these materials. The sulfone polymer was readily prepared by the action of 30% hydrogen peroxide in acetic acid on the sulfide polymer. The sulfone did not melt below its decomposition temperature, was insoluble, and had poorer thermal stability than the sulfide. This is similar to previous results obtained with Macallum polymers prior to the contract work.

In the case of the phenylene sulfoxide polymer some difficulties were encountered in its synthesis. First a synthesis which would give sulfoxide linkages free of sulfone was desired. This was found in a treatment of the sulfide polymer with 70% nitric acid in acetic anhydride at 0°C. A first attempt on a small scale appeared to be successful yielding a polymer in a 79% yield. Its infrared spectra showed a strong absorption near 1050 cm^{-1} (sulfoxide absorption). However, it did not show any absorption for a sulfone linkage, and its spectra differed from that of the phenylene sulfide polymer from which it was made at twenty different absorbent peaks. However, when this synthesis was repeated on a larger scale only partial oxidation of the sulfide to the sulfoxide was obtained. One sample showed only a weak sulfoxide absorption near 1050 cm^{-1} , and the other, on oxygen analysis, indicated that it contained at best 52% of the desired sulfoxide linkages.

Two possible explanations are suggested. One was the partial or total conversion of the acetic anhydride to acetic acid by moisture after the container was opened. If this happened the solvent might not be appropriate for the desired reaction under the conditions used. The second possibility was insufficient reaction time for the larger scale reactions. A fourth attempt was made subsequently using fresh acetic anhydride and a doubled reaction time. This procedure resulted in a material containing about 70% sulfoxide linkages. Therefore, an improvement was obtained but the reaction time is still insufficient.

In addition to oxidation of the polymers to the corresponding sulfoxide and sulfone, they were also studied to determine their stability to air oxidation and degradation at high temperatures. Table XIII indicates the stability of the polymers studied at comparable times. From the data it appears that the order of stability is heat treated >52% sulfoxide >sulfide \approx sulfide which is crosslinked to the extent of 1 crosslink per 10 repeating

TABLE XIII

Oxidative Resistance of Phenylene Sulfide Polymers

Run	1	2	3	4	5
Polymer	Heat Treated	Sulfide	Crosslinked	Sulfide	Sulfide
Treatment	72 hrs - 400°C	52% Sulfoxide	10 repeating units crosslink	None	Contains 4.3% CuBr
Weight Loss at 400°C in Air (%)					
Time (hrs)					
0.5			17.3		1.0
1.0	4.4		18.4	12.4	7.9
1.5		10.9		20.7	11.6
2.0	10.3		25.4		13.5
2.5		15.2		37.7	19.7
3.0					
4.0		20.3		47.1	19.8
6.0		39.0			23.6
8.0		53.8			26.4
12.0					38.6
18.0	63.2		97.5		
24.0			97.5		77.9
72.0	79.8	95.4		95.8	89.4

units. Of special interest is the result in run 5. It was suggested that the presence of cuprous bromide in the polymer might prove to be deleterious since copper has been known to be an oxidation catalyst. Therefore, a small portion of cuprous bromide was added to the same polymer used in run 4. We were surprised to find that instead of catalyzing oxidation the cuprous bromide appears to inhibit it to the point where the mixture is nearly as stable as heat treated material and surpasses that containing 52% sulfoxide linkages after 4.0 hours exposure.

In addition to the results in Table XIII some other runs were made in an open test tube in a heat treatment bath. These results, unlike those obtained in Table XIII from heating in a thermobalance, resulted in only a 22-25% weight loss after 72 hours at 400°C. In this latter case also, no degradation in properties occurred. The difference in the two situations may be that the thermobalance apparatus allowed a convection current to pass through it. Thus, volatile fragments would be rapidly removed from the reaction zone. In the open tube case this would not be true and therefore, the fragments may be able to interact with the residue again or at least act as a protective screen to exclude air from the remaining polymer.

Another difference exhibited by the open tube material was that although it was insoluble it did melt at 165-200°C. This is decidedly different from the heat treated materials obtained under argon or the air degraded materials from the thermobalance which are both infusible and insoluble.

In addition to the studies at 400°C lower temperatures were also investigated. After exposure for 3 days at 300°C in air no changes were observed in the polymer.

Crosslinking Studies

Two types of crosslinking have been studied. One variety is that due to chemical agents. Two possible crosslinking agents were discarded almost immediately. One, elemental sulfur, could induce formation of less stable polysulfide linkages in place of the sulfide linkages. Therefore, its use would be undesirable. A second agent, 1,4-benzenedithiol or its polymeric disulfide appeared to crosslink the polymer satisfactorily. However, it was found that by itself this reagent produced the same results that it did with the polymer. It apparently crosslinks itself and may not act on the sulfide polymer at all. Therefore, use of this material was dropped.

A third technique, which met with some success, involved treatment with chlorosulfonic acid at 160°C for 18 hours. This

reagent would introduce sulfone crosslinks. However, it appeared that the crosslink density produced was very non-uniform resulting in highly crosslinked "brick dust" type materials mixed with diphenyl ether soluble polymer. In addition the crosslink efficiency of this reagent was low¹⁰. Although the use of a solvent for the chlorosulfonic acid could improve the uniformity of the crosslinking, it would probably not improve the crosslink efficiency.

A much more successful technique than any of the preceding was a two step process. This involved bromination of the polymer to introduce the desired number of crosslink sites, and then treatment by a metal sulfide to introduce sulfide crosslinks. Both reactions resulted in essentially 80-100% yields of the desired substituent as indicated by analysis. There is some difficulty in bromination, however, if appreciable amounts of cuprous bromide are present. This material is preferentially oxidized by bromine and consequently fewer crosslink sites are introduced in the polymer than were intended. Therefore, careful removal of the cuprous bromide or the use of excess bromine to compensate for the amount of cuprous salt present is needed in order to get the desired amount of bromination of the polymer. The results of this investigation are presented in Table XIV. The first material was definitely too heavily crosslinked. The third material gave poor results due to non-uniform crosslink density. This fault was eliminated in the other two materials by the use of a solvent during bromination. As it can be seen a more uniform crosslink density produces a useful material. At present a crosslink density of one crosslink in 9-35 repeating units appears to give the best results. However, it is possible that even better results might be obtained with a crosslink density of one in five or one in fifty. This is being investigated. The two materials (numbers 2 and 4 in Table XIV) which gave the best results were crosslinked by mixing the brominated polymer with the amount of hydrated sodium sulfide equivalent to the bromine present in the polymer. This mixture was then placed in a press at 300°C and 20,000 pounds ram pressure for 24 hours. This technique of bromination with subsequent reaction with a metal sulfide can be used to produce a wide variety of crosslink densities with properties varying from essentially uncrosslinked material to that shown in line one of Table XIV.

In the course of this study two metal sulfides have been studied. Both of them, potassium and sodium sulfide, give comparable results. In addition the use of excess metal salt in the crosslinking does not appear to give better results. Further data on the polymers crosslinked in this manner will be presented in the discussion on the adhesive studies.

TABLE XIV

Preparation of Chemically Crosslinked Polymer

	<u>Crosslink Density (X/mer)</u>	<u>M.P. °C</u>	<u>DPO Sol. %</u>	<u>Molding Properties</u>
1.	2	>500	0.0	Not moldable- hard and brittle
2.	0.11	>400	0.0	Tough, flexible, and adheres well*
3.	0.10	245->300	92.0	Semimoldable- brittle
4.	0.07	>400	0.0	Tough, flexible, and adheres well*

* Crosslinked in press at 300°C and 20,000 lbs.

Two other materials have been found which show promise as crosslinking agents. One of these, benzaldehyde, when heated for 3 days at 150°C. with the polymer can produce a crosslinked material which can still be molded at high pressure, 20,000-40,000 pounds at 300°C. This material is tough and shows good adhesive strength. Benzaldehyde can also be used to crosslink at higher temperatures for shorter times but an excess must be used at temperatures above its boiling point due to evaporative losses.

The second material found recently was bis-(p-bromophenyl) disulfide. A mixture of 1,4-bisphenylthiobenzene and this disulfide was heated at 400°C under argon. This treatment produced a residue amounting to 21.4% by weight of the original charge. The residue had fairly good polymeric properties, and was very similar to heat treated phenylene sulfide polymer. The 1,4-bisphenylthiobenzene under the same conditions gives only a 0.79% residue with poor properties. Bis-(p-bromophenyl) disulfide heated alone under the same conditions gave a 27.4% residue again with poor properties. These results indicate that bis-(p-bromophenyl) disulfide is indeed crosslinking the 1,4-bisphenylthiobenzene to a high molecular weight network polymer. These two new crosslinking agents are being studied further also.

The second type of crosslinking studied was that induced by heat treatment. This study was originally undertaken in order to determine whether the thermally stable residue observed in thermogravimetric analysis¹¹ was a useful material. It was surprising to learn that heat treated phenylene sulfide polymer had decidedly improved properties in spite of a 25-40% weight loss¹². Previously it had been thought that a weight loss would result in a degradation of properties. Apparently this is not true with phenylene sulfide polymers.

Since this finding was especially interesting, a study of the volatile fragments of heat treatment was made in an effort to elucidate the reactions taking place. Two systems were used the volatiles being trapped in a dry-ice trap. A liquid nitrogen trap was tried but it liquified the argon used for the inert atmosphere. The first system studied was the polymer itself. The only identifiable product, using gas-liquid chromatography, was thiophenol. However, the other products were probably low molecular weight polymers such as dimers and trimers. Since elemental analysis showed a loss of bromine, heat treatment must also cause carbon-bromine bond cleavage. Further evidence for loss of bromine during heat treatment is the fact that the "linear" polymer and brominated polymer are self-extinguishing whereas the heat treated material is not.

In order to elucidate even further, the reactions induced by heat treatment, a model polymer system, 1,4-bisphenylthiobenzene,

was studied. On heating for 24 hours at 400°C under argon and analysis of the volatiles by gas-liquid chromatography several products were found in addition to the starting material. Four of these, benzene, thiophenol, diphenyl sulfide, and diphenyl disulfide, indicate carbon-sulfur bond cleavage which would result in substituted thiyl and phenyl radicals. In the case of a polymer then, these radicals could react with adjacent polymer producing crosslinks or volatilize off if their molecular weight is low enough.

A fifth material was also found in the volatiles from the model system. It was biphenyl. This material could result from a coupling of two phenyl radicals produced from carbon-sulfur bond cleavage or by a direct coupling of phenyl rings which is known to be possible at these temperatures¹³. Thus, this study suggests that two modes of crosslinking appear to be possible during polymer heat treatment. One is a radical attack by carbon-sulfur bond cleavage fragments and the other is a "biphenyl" coupling reaction. In addition, the analytical results and the loss of self-extinguishing properties of the polymer indicate the loss of bromine end groups during heat treatment.

As was mentioned previously beneficial results were obtained with the polymer by heat treatment at 400°C for 72 hours or at 500°C for 2-3 hours¹². The question arose as to whether further heating at these temperatures would lead to degradation. The question has already been partially answered for treatment at 500°C¹². At this temperature the polymer properties deteriorate after the initial enhancement. This deterioration is accompanied by further weight loss up to 24 hours. For longer heating periods at 500°C and for periods greater than 72 hours at 400°C the data in Table XV are pertinent. As it can be seen prolonged heating at 500°C under argon beyond 24 hours produces essentially no further change in weight or properties. However, the properties of this material are not very good and it is just short of brick dust. At 400°C, on the other hand, the results are very encouraging. These show that after the polymer has reached its optimum properties at 72 hours at 400°C, the polymer retains these properties with no further weight loss up to two weeks.

Because the polymer was so resistant to degradation at 400°C after initial heat treatment, some material treated for 72 hours at 400°C was heated further at 500°C to determine if it was also more resistant than non-treated polymer at this temperature. However, there appeared to be little difference between treated and non-treated materials after 24 hours.

In addition to the above studies heat treatments have been carried out on Macallum polymer, chemically crosslinked polymer, polymer containing 50% cuprous bromide, sulfone polymer, and

TABLE XV

The Effects of Prolonged Heat Treatment

<u>Time (hrs)</u>	<u>Temperature (°C)</u>	<u>Molded Film Properties</u>		
		<u>Weight Loss (%)</u>	<u>Flexibility and Toughness*</u>	<u>Adherence**</u>
0	500	0.0	2.5	4
2	500	16.1	4	5
6	500	26.3	3	5
24	500	44.4	1	1
45	500	49.4	1	1
120	500	46.4	1	1
240	500	47.6	1	1
0	400	0.0	1	1
20	400	16.1	1	1
40	400	21.7	2	2
72	400	29.1	6	5
144	400	28.6	6	5
240	400	33.1	6	5
288	400	~30	6	5

*Number Value

Meaning

1	Crumbly
2	Can bend slightly
3	Bends but breaks
4	Can crease but cracks
5	Creases but cracks on recreasing
6	Recreates without cracking

**Number Value

Meaning

1	No adherence
2	Some adherence
3	Resists removal
4	Difficult to remove
5	Cannot remove from glass
6	Cannot remove from glass or aluminum

sulfoxide polymer. The results are given in Table XVI. The Macallum polymer seems to behave in the same manner as the "linear" phenylene sulfide polymer as shown by Table XVI except that the property enhancements are not as great.

The crosslinked polymers were of interest since they showed a property enhancement but did so without melting. Thus, it should be possible to prepare an article by thermoplastic fabrication followed by a chemical crosslinking cure. The resulting material could then be further improved by heat treatment without fear of loss of shape due to melting which would occur in the case of the "linear" polymer.

The cuprous salt containing polymer gave poor results for two reasons. One was the presence of a heterogeneous inorganic phase which was not completely bound by polymer. The second was an apparent reaction of cuprous bromide with the polymer during heat treatment producing copper metal. This reaction could possibly have deleterious effects on the polymer producing the results observed.

The last two polymers are of interest also since they represent oxidized forms of the sulfide polymer. Comparison with Table XV, indicates that the sulfone polymer is less stable than the sulfide while the sulfoxide polymer behaves very much like phenylene sulfide polymer.

Finally an attempt has been made to scale up the heat treatment process. At first this was unsuccessful due to the inability to completely remove the air from the sample by argon flushing. However, when the reactions were run under a vacuum, 5-10 gram samples of polymer could be treated at 400°C yielding the same improved properties with the same weight loss as the 0.5 gram sample runs listed in Table XV.

Applications Investigations

Preliminary investigations have been conducted on possible applications of the phenylene sulfide polymer. It was found that fibers can be readily drawn from the melt of higher molecular weight polymers. However, when a small sample was studied for the melt spinning properties of the polymer no conclusive results were obtained. This was due to the small size of the sample and its very good adhesive properties which prevented it from draining from the melt spinning apparatus. However, the investigator felt that success could be obtained on a larger sample.

TABLE XVI

Heat Treatment of Modified Phenylene Sulfide Polymers

<u>Polymer</u>	<u>Time (hrs)</u>	<u>Temperature (°C)</u>	<u>Weight Loss (%)</u>	<u>Molded Film Properties</u>	
				<u>Flexibility and Toughness*</u>	<u>Adherence**</u>
Macallum	0	400	0.0	2	5
	72.0		23.8	2	4
Crosslinked 9.5/1	0	400	0.0	2.5	5
	72.0		41.0	4	5
15.5/1	0	400	0.0	3.5	4.5
	72.0		36.9	5	5
Linear + 50% CuBr	0	400	0.0	1	1
	72.0		44.9	1	1
Sulfone	0	400	0.0	1	1
	72.0		34.9	1	1
Sulfoxide	0	400	0.0	1	1
	72.0		26.0	2	6

* Same as per Table XV

** Same as per Table XV.

No real laminate work has been carried out by this group. However, work at Wright Field has shown that no difficulty was encountered in saturating glass cloth with the polymer and that it wets the fibers well.

A fair amount of effort has been expended in studying the adhesive properties of the polymer. This study was mainly concerned with finding the treatment or treatments of the test bars and polymer which would give the best results.

In our initial work some difficulty was encountered when phosphate or chromate etch solutions¹⁴ were used. When heat treatments were carried out subsequent to bonding the test bars, the polymer in the etched region appeared to have been attacked while polymer outside this region was not.

Apparently either the etch solution left a residue or acted on the metal in such a way that even after removal of the etch solution by rinsing and drying the polymer was degraded in that region at heat treatment temperatures. This difficulty was eliminated, however, by the use of an aqua regia etch¹⁴, which did not appear to act in the above manner.

The results of the adhesive investigation are given in Tables XVII - XIX. As it can be seen, there is a great deal of fluctuation which is no doubt due to the method of testing and our developing technique.

Table XVII represents results from linear polymers. The range of bond strengths in the lap shear test was 200-1620 psi. It should be noted that with the exception of the first entry the bond strengths are increasing as our technique has developed. At present, however, bond strengths are about half that obtained at Wright Field on similar polymers.

Table XVIII lists the results for chemically crosslinked polymer. Here the range of bond strengths is 226-2740 psi. Again some scatter in the results is present. In comparing runs 3-6 it can be seen that the use of either metal sulfide studied or the use of an equivalent amount or excess metal sulfide seems to give about the same results. With runs 7-11 and 12-15 the results of improving technique can be seen in the higher and more consistent bond strengths of these samples compared to earlier ones. At present the crosslink density yielding the best bond strength for the bromination-metal sulfide technique has not been determined. From the data in Table XVIII a crosslink density of 1 crosslink/34 repeating units would appear to be best. However, runs 1-6 will have to be repeated to confirm this. In addition, the results in Table XVIII may be affected by the molecular weight of the polymer being crosslinked.

TABLE XVII

Adhesive Properties of Linear
Phenylene Sulfide Polymer

<u>Run</u>	<u>D.P.^a</u>	<u>Steel</u>	<u>Etch</u>	<u>Bond Strength</u> <u>(psi)</u>
1	60	17-7	None	1620
2	60	17-7	Phosphate	364
3	52	17-7	Aqua Regia	208
4	62	17-7	Aqua Regia	500
5	98	17-7	Aqua Regia	880
6	98	17-7	Aqua Regia	1060
7	101	17-7	Aqua Regia	1220
8	105	17-7	Aqua Regia	640
9	105	17-7	Aqua Regia	930
10	101 ^b	17-7	Aqua Regia	623
11	66 ^c	17-7	Aqua Regia	560

a. From melt viscosity

b. Contains 4.3% CuBr

c. 52% Sulfoxide.

TABLE XVIII

Adhesive Properties of CrosslinkedPhenylene Sulfide Polymers^a

Run	Agent	<u>Crosslink</u>			<u>Bond Strength</u>
		Density (mers/link)	<u>D.P.</u> ^b		
1	Na ₂ S·5H ₂ O	9.5	16		620
2	Na ₂ S·5H ₂ O ^c	15	16		226
3	Na ₂ S·5H ₂ O	15.5	48		550
4	Na ₂ S·5H ₂ O ^c	15.5	48		605
5	K ₂ S ^c	15.5	48		780
6	K ₂ S ^d	15.5	48		510
7	K ₂ S ^c	27	105		531
8	K ₂ S ^c	27	105		1071
9	K ₂ S ^c	27	105		1270
10	K ₂ S ^c	27	105		1440
11	K ₂ S ^c	27	105		2260
12	K ₂ S ^c	34	105		796
13	K ₂ S ^c	34	105		1230
14	K ₂ S ^c	34	105		2100
15	K ₂ S ^c	34	105		2740

a. Steel used was 17-7 and etch was aqua regia

b. From melt viscosity on polymer prior to crosslinking

c. 100% excess

d. 500% excess.

TABLE XIX

Adhesive Properties of Heat Treated

Phenylene Sulfide Polymer

Run	Heat Treatment Conditions		<u>D.P.^a</u>	Steel	<u>Etch</u>	Bond Strength (psi)
	Time (hrs)	Temp. (°C)				
1 ^b	69	400	60	316	None	200
2 ^b	72	400	36	316	None	1860
3	72	400	20	17-7	None	186
4 ^b	72	400	35	17-7	None	560
5 ^b	72	400	35	17-7	Phosphate	Too low to measure
6	72	400	20	17-7	Wire Buff	230
7	72	400	38	17-7	Wire Buff	175
8	144	400	105	17-7	Wire Buff	650
9	72	400	135	17-7	Wire Buff	470
10	72	400	20	17-7	Aqua Regia	1095
11	72	400	38	17-7	Aqua Regia	1800
12	144	400	105	17-7	Aqua Regia	2360
13	72	400	135	17-7	Aqua Regia	1238
14 ^{b,c}	72	400	64	17-7	Aqua Regia	1280
15 ^b	72	400	64	17-7	Aqua Regia	326
16 ^b	72	400	64	17-7	Aqua Regia	179
17 ^{b,c}	72	400	64	17-7	Aqua Regia	1160

a. From melt viscosity prior to heat treatment

b. Heat treated after bond formed

c. Molded after bond heat treated.

Table XIX presents the results for heat treated polymers. The range of bond strengths here was 186-2360 psi. Again with the exception of run 2 bond strengths have improved with improving technique. Two techniques were used to prepare heat treated bonds. One involved heat treating the polymer under the conditions indicated in Table XIX followed by bonding the test bars. The other method reversed these two steps and involved heat treating the bonded samples. From Table XIX it appears that either technique gives essentially the same results provided the data in runs 14-17 are taken into consideration. Runs 14 and 17 were placed in a press at 35,000 pounds pressure at 300°C for fifteen minutes after heat treatment, whereas runs 15 and 16 were not. From the bond strengths obtained it is apparent that post molding after heat treatment of bonded samples is beneficial. Apparently gas pockets or cavities can form during heat treatment which should be squeezed out in order to have the bonded area filled with polymer.

Another piece of information provided by Table XIX is the effect of metal surface treatment. No treatment gave scattered results as expected. However, when the surface was treated the following order of bond strengths was produced, aqua regia etch > wire buff > phosphate etch. As was mentioned before, the phosphate etch seems to cause degradation of the polymer if heat treated after bonding. The result of bonding phosphate etched metal with heat treated polymer is not known.

Of the three types of adhesives studied the crosslinked polymer and the heat treated polymer appear to give the best results at room temperature.

An attempt was made to heat treat bonded samples in air in a muffle furnace at 425°C. However, apparently due to the creation of cavities during the melting phase of the treatment, air came into contact with the bulk of the polymer and degraded it resulting in very weak bonds, 0-590 psi. Therefore, heat treatment even of bonded samples should be conducted in an inert atmosphere or a vacuum.

III. CONCLUSIONS

The following are the conclusions that can be drawn from our data:

(1) The best technique devised for bis-(p-bromophenyl) disulfide synthesis is the reaction of bromine with thiophenol without solvent.

(2) The preferred synthesis of monomer is the reaction of copper dust, fresh or electrolytic, with a 50% excess of bis-(p-bromophenyl) disulfide in an n-alkyl alcohol at 119-140°C under pyridine catalysis.

(3) The presence of air does not seem to influence the result of polymerization greatly but may change the chemical nature of the polymer somewhat.

(4) Better polymer results if excess bromine is used to make bis-(p-bromophenyl) disulfide.

(5) The preferred method of polymerization is heating of the solid monomer at 200°C under an inert atmosphere with agitation.

(6) Light does not appear to catalyze polymerization but does catalyze monomer formation.

(7) From the standpoint of ease and speed of handling, concentrated hydrochloric acid extraction is preferred for isolation and purification of polymer by removal of cuprous bromide. However, if a "linear" polymer free of cuprous bromide is desired, diphenyl ether extraction is the only method available.

(8) The process for preparation of phenylene sulfide polymer can be scaled up to a pound scale with little difficulty except for a heat transfer problem which occurs during polymerization.

(9) The best solvents for phenylene sulfide polymer have boiling points in excess of 200°C and have cohesive energy densities of 90-100.

(10) Melt viscosity and solution viscosity can be related to molecular weight by the relations:

$$\log M_n = 0.147 \log \eta_{303} + 1.32$$

$$\log M_n = 2.35 \log \frac{\eta_{sp}}{C} + 3.47$$

(11) In order to exhibit optimum properties the polymer must have a melt viscosity in excess of 1.3×10^3 poises.

(12) Phenylene sulfide polymer appears to have good solvent resistance.

(13) Phenylene sulfone polymer does not have useful properties.

(14) The stability of phenylene sulfide polymers to air at 400°C is in the order heat treated polymer > cuprous bromide containing polymer > 52% sulfoxide polymer > chemically crosslinked polymer \approx linear polymer. At 300°C no degradation occurs up to 3 days in air.

(15) Cuprous bromide appears to inhibit air degradation of phenylene sulfide polymer.

(16) Phenylene sulfide polymer can be successfully cross-linked to a variety of crosslink densities by bromination followed by treatment with an alkali metal sulfide.

(17) Benzaldehyde and bis-(p-bromophenyl) disulfide appear to be useful as crosslinking agents.

(18) Crosslinking by heat treatment appears to be caused chiefly by radical attack of carbon-sulfur bond cleavage fragments with some "biphenyl" coupling.

(19) Heat treatment of linear or crosslinked polymer at 400°C results in enhanced polymer properties after 72 hours inspite of a 25-40% weight loss. Further heating at 400°C results in no change.

(20) At 500°C properties are enhanced during the first few hours and then deteriorate to a brick dust type material after 24 hours.

(21) Five-ten gram samples of polymer can be heat treated in a vacuum.

(22) The polymer should be capable of melt spinning into fibers.

(23) Laminates can be made from phenylene sulfide polymer.

(24) Adhesive bond strengths of the various modifications of phenylene sulfide polymer that have been obtained are linear 200-1620 psi, crosslinked 226-2740 psi, and heat treated 186-2360 psi. Strengths are improving.

(25) Heat treatment above 350°C in air is not beneficial.

IV. EXPERIMENTAL

With the exception of those preparations given in detail below, all of the techniques used during the investigations described above have been presented in the annual reports on Phenylene Sulfide Polymers WADD TR-61-139 and ASD-TDR-62-322.

Monomer Synthesis

Cuprous p-Bromothiophenoxide¹⁵. A mixture was made up composed of 128 g (0.341 moles) of bis-(p-bromophenyl) disulfide, 34 g (0.598 moles) of freshly prepared copper dust or electrolytic copper dust, 1.5 l. of n-butyl alcohol, and 5 ml of pyridine. This was placed in a 3 l. three-necked flask fitted with a reflux condenser and stirrer. The stirred reaction mixture was heated at reflux for 5.5 days. Then the precipitate was filtered, washed with benzene, and dried for 64 hours at 80°C under vacuum. Yield was 150 g or 99.8%.

Analysis

	C	H	Br	Cu
Calculated	28.52%	2.01%	31.62%	25.14%
Found	28.36%	1.72%	31.67%	24.25

The fresh copper dust was made as follows: To 149 g (0.299 moles) of copper sulfate pentahydrate in one liter of water was slowly added 41 g (0.314 moles) of zinc dust with stirring. After 15-20 minutes 10 ml of concentrated hydrochloric acid was added to remove any excess zinc. The mother liquor was decanted off and the residue washed with water, acetone, and then n-butyl alcohol decanting off the liquid each time. The fresh copper dust still wet with n-butyl alcohol was then added to the reaction mixture above.

Polymerization

Into a clean dry glass ampoule was loaded 340 gms of cuprous p-bromothiophenoxide. The ampoule was evacuated and filled with argon three times and then sealed. Then the ampoule in a steel jacket was placed in an oven at 200°C. At least once every 24 hours the ampoule was removed and rotated or shaken to mix the contents. After 2 days the ampoule was cooled and opened. The crude polymer was taken up in 25 l. of diphenyl

ether and the resulting mixture brought to a boil. When boiling, the mixture was suction filtered through a heated büchner funnel. The filtrate was reheated to boiling to redissolve any precipitate and poured into 75 l. of acetone in a beaker with vigorous stirring. The precipitate was filtered off, washed with acetone, and dried overnight at 125°C in a vacuum oven. Yield was 116 gms or 84.2%, M.P. 280-285°C.

Analysis

	Calculated		Found
	Infinite D.P.	D.P. = 75	
C	66.65	66.00	66.10
H	3.73	3.69	3.64
S	29.65	29.35	29.20
Br	-----	1.00	1.09
Cu	-----	0.00	0.00

Chemical Properties of the Polymer

Synthesis of Phenylene Sulfone Polymer. To 2.5 gms (0.0232 mer weights) of phenylene sulfide polymer and 1 ml of sulfuric acid in 75 ml of glacial acetic acid at 75°C, 10 ml of 30% hydrogen peroxide was added dropwise with stirring over a one hour period. After the addition was completed, the reaction mixture was stirred 5 hours at 75°C. Then it was poured into 300 ml of water and allowed to stand for several hours. The polymer was filtered off and dried. Yield was 3.2 gms or 98.9% of phenylene sulfone polymer which did not melt.

Analysis of Sulfone

	Calculated	Found
C	46.10	58.76
H	2.58	3.40
S	20.50	21.75
O	29.70	15.09
Br	1.00	1.00
Cu	0.00	0.00

The analysis indicates a 51% conversion of sulfide to sulfone linkages using a procedure known to give sulfones with Macallum polymer.

Synthesis of Phenylene Sulfoxide Polymer. To 5.000 gms (0.0463 mer weights) of phenylene sulfide polymer in 200 ml of acetic anhydride at 0°C was added dropwise with stirring 1.72 ml (0.0356 moles) of nitric acid (70%) in 50 ml of acetic anhydride. The resulting mixture was stirred 48 hours at 0-5°C. Then it was poured into ice-water, neutralized with sodium carbonate, and filtered. Yield was 4.90 gms or 85.4% of phenylene sulfoxide polymer, M.P. 286-290°C. Infrared indicates no sulfone or sulfide and has a strong sulfoxide absorption near 1050 cm^{-1} .

Analysis of Sulfoxide

	Calculated	Found
C	56.45%	63.46%
H	3.15%	3.98%
S	25.10%	23.86%
O	12.52%	5.81%
Br	1.60%	1.62%
Cu	1.26%	1.27%

The analysis indicates a 46% conversion of sulfide to sulfoxide linkages.

Crosslinking Studies

Bromination of Linear Phenylene Sulfide Polymer¹⁶. To 2.009 g (0.0186 mer weights) of linear phenylene sulfide polymer (diphenyl ether soluble) (M.P. 265-270°C) was added 10 ml (0.195 moles) of bromine. The reagents were allowed to stand overnight. Then the excess bromine was evaporated off. Yield was 4.99 gms (M.P. 300-310°C), a weight increase indicating the addition of about two bromine atoms per repeating unit. Elemental analysis showed it to be actually 1.67 bromine atoms per repeating unit (52.8% bromine).

The above process was repeated using 1.57 g (0.0146 mer weights) of polymer and 0.075 ml (0.00146 moles) of bromine. This resulted in the introduction of 0.096 bromine atoms per repeating unit or one in ten repeating units as shown by the weight gain and elemental analysis. Yield was 1.69 g (M.P. 267-276°C) (6.6% bromine).

Crosslinking Brominated Polymer. The brominated polymer is intimately mixed with an amount of $\text{Na}_2\text{S} \cdot 5\text{H}_2\text{O}$ equivalent to the bromine in the polymer. This would be 1.15 gms for each 10 gms of polymer with one bromine in 9.5 repeating units. The

mixture is then heated for 10-15 hours at 300°C. This process can be carried out as a curing process in the preparation of adhesive bonds.

The use of 100% excess of the $\text{Na}_2\text{S} \cdot 5\text{H}_2\text{O}$ over that which is required has been found to enhance the strength of adhesive bonds made by this method. Potassium sulfide has been found to give results superior to the sodium salt for adhesive purposes.

Analysis of Chemically Crosslinked Polymer

	Calculated (1.5-S per repeating unit)	(1-S, 3 ϕ - ϕ x-link per 12 repeating units)	Found
C	46.60	61.60	61.92
H	1.63	3.15	3.18
S	51.70	29.60	29.26
Cu	0.00	0.00	0.00
Br	0.00	5.64	5.64

The ϕ - ϕ crosslinks may have arisen through an oxidation reduction reaction involving the sodium sulfide and the aryl bromide groups.

Benzaldehyde. To 1.00 gms (0.0093 mer weights) of phenylene sulfide polymer in a 250 ml round bottom flask was added 0.1 ml of benzaldehyde. After thorough mixing, the resulting mixture was heated to 150°C and kept at this temperature for 92 hours. The resulting crosslinked polymer only partially melted (less than 35%) from 200-300°C. On molding between aluminum pans at 300°C, it appeared to adhere well. The polymer appears to have a slightly non-uniform crosslink density resulting in the partial melting observed.

Analysis of Benzaldehyde Crosslinked Polymer

	Calculated	Found
C	62.08	62.18
H	3.23	3.56
S	28.00	27.71
O	3.34	3.15
Cu	0.25	0.25
Br	3.15	3.15

Heat Treatment

A 1.4249 gm sample of linear phenylene sulfide polymer was weighed out into a 10 ml beaker. This was placed in a tube and capped with a top containing gas inlet and outlet tubes. The pyrolysis tube described above was then connected to an argon tank and flushed with argon for 30 seconds at a rapid flow rate. Then the flow rate was reduced to 1-2 bubbles per second in a bubbler tube. The pyrolysis tube was then immersed in a stirred bath at 400°C such that the beaker in the tube was below the surface of the bath. After the designated time interval, in this case 3 days, the tube was removed from the bath and allowed to cool. Once cool the argon flow was stopped and the sample reweighed. Yield was 1.0460 gms or a weight loss of 26.6%. The black glassy material after being cut away from the smashed beaker did not melt and was insoluble in diphenyl ether. Its thin film properties using the number value system on page 38 was flexibility and toughness 6, and adherence 5. The films were also transparent.

Analysis

	Calculated (1 Sulfur crosslink per 6 repeating units)	Found
C	63.70%	63.86%
H	3.27%	3.22%
S	33.10%	32.99%
Br	0.02%	0.01%
Cu	≤0.02%	≤0.02%

Applications Studies

Procedure for Preparing Adhesive Test Samples. The metal bars 0.062" x 1" x 4" were first washed in methyl ethyl ketone. Then they were scoured with water and scouring powder. After rinsing, the bars were immersed about 2 inches deep in the etch bath. The etch conditions were 2 minutes and 90°C for phosphate etch and 2 minutes and room temperature for aqua regia. Then the bars were removed, rinsed thoroughly with distilled water, and dried 10 minutes at 110°C and 25 mm Hg. The polymer was placed between the dried bars so that a half inch overlap would occur and the sample was then placed in a press at 300°C to form the bond. For linear and heat treated material the samples remained in the press for 15-20 minutes at 5,000 lbs. pressure for linear

and 35,000 for heat treated. For crosslinking, the brominated polymer and metal sulfide remained at 300°C and 5,000 lbs. for 15 hours.

Samples

The following samples were sent to Wright-Patterson Air Force Base, Ohio.

<u>Polymer</u>	<u>Quantity</u>	<u>M.P.</u> <u>(°C)</u>	<u>Properties</u>		
			η 303 (poises)	DPO Sol. (%)	η_{rel}
Linear-Film (Film)	<1 gm	280-285	7×10^4	100	-----
Heat Treated	<1 gm	>600	-----	---	-----
72 hrs -400°C	<1 gm	>600	-----	---	-----
Chemically Crosslinked	<1 gm	>400	-----	---	-----
Heat Treated 72 hrs -400°C Glass cloth laminate	3 samples	>600	-----	---	-----
Linear- Glass plate laminate	1 sample	262-265	1.5×10^3	100	1.185
Heat Treated 72 hrs -400°C Glass plate laminate	1 sample	>600	-----	---	-----
Linear	225 gms	282-287	2×10^3	85-90%	1.191
Linear	225 gms	285-287	5×10^4	86-88%	-----
Sulfoxide (40-50%)	1.2 gms	280-288	2.4×10^3	---	-----

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Rpt No. ASD-TDR-62-322, Pt II. PHENYLENE SULFIDE POLYMERS. Interim report, Dec 62, 52p. incl illus., tables, 15 refs.

Unclassified Report

The investigation of phenylene sulfide polymers has been divided into seven areas of endeavor. These are monomer synthesis, polymerization studies, large scale preparations, physical properties of the linear polymer, chemical properties of the polymer, cross-

(over)

linking studies, and applications. With improvements in the monomer synthesis polymerization, one pound batches of polymer can be made. Once made, the polymer has a degree of polymerization in excess of 100 and is inert to air up to 300°C. It can be chemically crosslinked to improve its stability at 400°C in air or heat treated to not only improve its thermal and oxidative stability at 400°C but to improve its properties as well. The polymer can form fibers from the melt and be used in coatings and laminates. However, its most thoroughly investigated property is its adherence. Bond strengths up to 2700 psi have been obtained on 17-7 stainless steel. It also adheres well to glass and aluminum.

1. Polymers
2. Inorganic Anions
- I. AFSC Project 7340, Task 734004
- II. Contract AF33(616) 7251
- III. Dow Chemical Co., Midland, Mich.
- IV. Harry A. Smith
- V. Not aval fr OTS
- VI. In ASTIA collection

Aeronautical Systems Division, Dir/Materials and Processes, Nonmetallic Materials Lab, Wright-Patterson AFB, Ohio.
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